

The crystal structure of triploidite and its relation to the structures of other minerals of the triplite-triploidite group

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Auszug

Für Triploidit, $(\text{Mn,Fe})_2\text{PO}_4(\text{OH})$, von Branchville, Connecticut, wurden die Gitterkonstanten $a = 12,366 \text{ \AA}$, $b = 13,276 \text{ \AA}$, $c = 9,943 \text{ \AA}$, $\beta = 108,23_0^\circ$ und die Raumgruppe $P 2_1/a$ gefunden. Die Triploiditstruktur beruht auf der Struktur von Triplit als Substruktur. Eine Fourier-Synthese dieser Substruktur mit den Strukturamplituden des Triploidits und den Amplitudenvorzeichen der Triplitstruktur führte zu einem brauchbaren Ausgangsmodell. Die Verfeinerung mittels der Methode der kleinsten Quadrate verbesserte den R -Wert von 39% auf $5,7\%$ für 769 meßbare Interferenzen.

Die Triplit-Triploidit-Gruppe kann in zwei Untergruppen isotyper Minerale eingeteilt werden: Die eine Untergruppe enthält Triplit–Zwieselit, die andere Triploidit–Wolfeit, Wagnerit und vielleicht Sarkinit. Die Strukturen von Triplit und Triploidit sind in vieler Beziehung ähnlich. Sie unterscheiden sich hauptsächlich durch Anordnung der (F,OH)-Lagen und durch geringe Verschiebungen der Atome. Beides zusammen bedingt Änderungen in der Umgebung der (F,OH)-Lagen, wodurch eine Verringerung der Abstoßung zwischen den Metall- und den Hydroxylwasserstoff-Atomen in der Triploiditstruktur möglich wäre.

Abstract

Crystals of triploidite, $(\text{Mn,Fe})_2\text{PO}_4(\text{OH})$, from Branchville, Connecticut, were found to have space group $P 2_1/a$ and cell dimensions $a = 12.366 \text{ \AA}$, $b = 13.276 \text{ \AA}$, $c = 9.943 \text{ \AA}$ and $\beta = 108.23_0^\circ$. Triploidite is based on a triplite substructure. A Fourier synthesis of the substructure, using the F_o 's of the triploidite substructure and the signs given by the triplite model, suggested a beginning model. Three-dimensional least-squares refinement reduced the discrepancy index R of this model from 39% to 5.7% for the 769 measurable reflections.

The triplite-triploidite group can be divided into two subgroups of isotypic minerals: one subgroup contains triplite-zwieselite; the other is composed of triploidite-wolfeite, wagnerite and probably sarkinite. The triplite and triploidite structures are similar in most respects. The primary differences between the two

lie in the ordering of the F,OH sites and in small shifts in atomic positions. The coupling of these differences gives rise to a change in the environment of the F,OH sites which probably allows the repulsion between the metal and OH-hydrogen atoms to be reduced in the triploidite structure.

Introduction

The mineral triploidite, $(\text{Mn,Fe})_2\text{PO}_4(\text{OH})$, was discovered by BRUSH and DANA (1878*a*). The name was chosen to reflect its marked resemblance to triplite, $(\text{Mn,Fe})_2\text{PO}_4\text{F}$, with which it is often closely associated in granite pegmatites.

The two minerals, triplite and triploidite, have similar compositions, but are not isotypic. Since F and OH have approximately the same size and bonding characteristics, they commonly substitute for each other in minerals. In some cases the substitution is limited; in others a complete compositional series is found between an F end member and an OH one. Except when the amount of F or OH present is quite large and the slight size difference becomes important or when the polar nature of OH plays a significant role in the structure, the substitution of F and OH for each other does not alter the general nature of the structure, and isotypy is found between the F-rich and OH-rich material. However, this is not true for triplite and triploidite. No series between them is known in nature, and, as first pointed out by KOKKOROS (1938), they are not isotypic.

Since the crystal structures were not known for either of these interesting, non-isotypic minerals, an investigation of them was undertaken. This is one of a series of publications reporting the results (WALDROP, 1968*a*, 1968*b*, 1969). In this paper the study of triploidite is discussed.

Experimental data

Cell dimensions and space group

The unit-cell dimensions and space group determined by KOKKOROS (1938) were based on Weissenberg photographs of iron-rich triploidite, or wolfeite, $(\text{Fe,Mn})_2\text{PO}_4(\text{OH})$, from Hagendorf, Bavaria. His results were confirmed by the studies of RICHMOND (1940) on triploidite from Branchville, Connecticut, and those of FRONDEL (1949) on wolfeite from the Palermo mine, North Groton, New Hampshire. The results shown here are in agreement with these previous studies.

Dr. CLIFFORD FRONDEL of Harvard University provided single crystals of triploidite from Branchville, Connecticut, for the investiga-

tion. Material from this locality was found by BRUSH and DANA (1878*b*) to have a composition of $\text{Mn}_{1.5}\text{Fe}_{0.5}\text{PO}_4(\text{OH})$ and a specific gravity of 3.697.

Spacing values for 83 reflections from $h0l$, $hk0$ and $0kl$ back-reflection Weissenberg photographs were refined by least-squares to give these cell dimensions:

$$\begin{aligned}a &= 12.366 \pm 0.001 \text{ \AA}, \\b &= 13.276 \pm 0.002 \text{ \AA}, \quad \beta = 108.230 \pm 0.004^\circ \\c &= 9.943 \pm 0.001 \text{ \AA}.\end{aligned}$$

There are 16 formula units per cell.

Complete sets of b -axis and c -axis precession photographs showed systematic absences of $h0l$ for h odd and of $0k0$ for k odd. This corresponded to the space group $P2_1/a$.

Intensity measurements

The crystal fragment chosen for intensity measurement was prismatic parallel to c , bounded by $\{100\}$ and $\{120\}$. The approximate dimensions were $0.18 \times 0.16 \times 0.19$ mm.

The reflection intensities were measured by the fixed-counter, rotating-crystal method on a diffractometer with equi-inclination Weissenberg geometry. The detector was a proportional counter with associated pulse-height discrimination circuitry. Filtered $\text{FeK}\alpha$ radiation was used.

All reflections accessible with the detector were measured along the positive b axis. Then the intensities were averaged in pairs according to the symmetry $P2_1/a$. Of the 1417 unique reflections measured, 502 had intensities below the limit of measurement I_{\min} ; for these a value of $I = \frac{1}{3} I_{\min}$ was assigned, as suggested by HAMILTON (1955).

After the intensities were corrected for Lorentz and polarization effects, absorption corrections were computed using the program GNABS written by Dr. CHARLES W. BURNHAM. Then the structure factors, F_o , corresponding to the intensities were put on an absolute scale by the WILSON (1942) method.

Determination and refinement of the structure

One obvious characteristic of the reflections, noted first on the precession photographs, is that they can easily be divided into two groups: strong substructure ones and weak complement-structure

ones. The substructure reflections are found on levels with k even and have indices for which

$$hkl: h + \frac{1}{2}k + l = 2n$$

and

$$h0l: h = 2n.$$

BUERGER (1959) has suggested that when a substructure is present, it is often helpful to discover its details first before considering the structure within the entire unit cell. For triploidite the substructure reflections defined a cell with dimensions

$$a_s = a, \quad b_s = b/2 \quad \text{and} \quad c_s = c$$

and with symmetry $I2/a$. The cell dimensions and also the intensities of the substructure reflections displayed a striking resemblance to those of triplite. The analogy between triplite and the triploidite substructure was further suggested by the similarities between their Patterson functions $P(xyz)$; a good correspondence was found between the two in peak location and, for most peaks, in peak height.

So it appeared desirable to test the extent of their similarity. Structure factors were calculated from coordinates and isotropic B values for triplite, using the model obtained after the completion of the first phase of least-squares refinement on triplite. The discrepancy index R with these triplite F_c 's and the triploidite substructure F_o 's was 30%. A Fourier synthesis, calculated with the substructure F_o 's and the signs given by the triplite model, was identical with a synthesis calculated for triplite except that each peak corresponding to an OH-oxygen atom was split into two peaks separated by about 1.6 Å.

All the evidence seemed to suggest that the triploidite structure was made up of two triplite subcells which alternate in the b direction. It appeared likely that the primary difference between the arrangement of atoms in the two subcells was in the locations of the OH's; thus it was assumed that in the substructure Fourier synthesis, one peak of each OH pair corresponded to the OH location in one subcell and the second peak to the OH location in the other subcell. So the beginning structural model adopted for triploidite was that of triplite with a doubled b axis, but with the positions for the OH-oxygen atoms suggested by the triploidite substructure Fourier. This model gave an R of 39%.

Each triplite equipoint corresponded to four equipoints in the triploidite model, due to the doubling of the triplite b axis and to the

decrease in multiplicity of the general position from 8 in $I2/a$ to 4 in $P2_1/a$. Since the starting model had symmetry $I2/a$ except for the OH sites, high correlation would be expected among the variables of each set of four equipoints related by pseudosymmetry elements of $I2/a$. Because of this, it appeared desirable in the early stages not to use full-matrix refinement. Instead, the 32 atoms of the asymmetric unit were divided into four groups of 8 atoms each. The atoms assigned to a group were chosen so that no two atoms in the group would be related by a pseudosymmetry element; thus each group contained two metal atoms, one P, four O's and one OH. Then only interactions between atoms of a group were allowed to influence parameter changes; all elements of the normal-equation matrix which represented interactions between atoms of different groups were set to zero before the matrix was inverted.

The least-squares refinement program used was SFLSQ3 by Dr. CHARLES T. PREWITT. Each cycle contained the corrections for anomalous scattering given by CROMER (1965).

To begin the refinement of the proposed triploidite model, 769 reflections were included, all those for which $I > 1.2 I_{\min}$. Each of the 333 substructure and the 436 complement-structure F_o 's was given a unit weight. The scale factor and coordinates were varied for one cycle.

When weighting the F_o 's in refinement, one usually lets the F_o 's whose values are known most precisely (normally those of larger magnitude) have the greatest influence. The procedure, however, has disadvantages when a substructure is present. In triploidite the more intense substructure reflections give information primarily about the substructure, or average structure, while the weaker complement-structure reflections result from the shifts of the atoms from the average positions. Thus the weighting scheme to be used should not negate the influence of the important, though less precisely known, complement-structure F_o 's.

For this reason the substructure F_o 's were removed, and the selected complement-structure F_o 's were used to refine the scale factor and coordinates. The structure factors were weighted according to a scheme suggested by WUENSCH (1964). First R was calculated as a function of F_o . Then a weighting function was used for which the product of the weight and R is a constant for all F_o 's. After convergence of the scale factor and coordinates, the isotropic-temperature factors, B , were varied for two cycles.

For the remainder of the refinement, separate Wuensch-type weighting schemes were adopted for substructure and complement-structure reflections. Then, to give the complement-structure F_o 's an increased influence, the weight of each substructure F_o was reduced by one half.

The selected substructure reflections, except for eleven which appeared to suffer large extinction effects, were again added to the set of structure factors to be refined. The scale factor and coordinates

Table 1. *Positional coordinates and isotropic temperature factors for triploidite resulting from refinement with reflections for which $I > 1.2 I_{\min}$*

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
M(1)	0.1874	0.0003	0.4784	0.0003	0.1881	0.0004	0.44 Å ²	0.06 Å ²
M(2)	0.1970	0.0004	0.9968	0.0003	0.2100	0.0005	0.82	0.07
M(3)	0.3047	0.0004	0.7517	0.0003	0.2958	0.0005	0.75	0.07
M(4)	0.3184	0.0003	0.2696	0.0003	0.3085	0.0005	0.47	0.07
M(5)	0.0974	0.0003	0.0710	0.0003	0.4660	0.0004	0.22	0.07
M(6)	0.0837	0.0003	0.5747	0.0003	0.4448	0.0004	0.24	0.06
M(7)	0.3940	0.0003	0.6746	0.0003	0.0342	0.0004	0.26	0.06
M(8)	0.4232	0.0003	0.1781	0.0003	0.0448	0.0004	0.53	0.06
P(1)	0.0778	0.0007	0.8225	0.0009	0.3789	0.0011	0.42	0.16
P(2)	0.0741	0.0007	0.3274	0.0009	0.3823	0.0012	0.38	0.16
P(3)	0.4229	0.0007	0.4230	0.0009	0.1142	0.0011	0.34	0.16
P(4)	0.4238	0.0007	0.9285	0.0009	0.1199	0.0011	0.37	0.16
O(1)	0.0475	0.0009	0.4132	0.0012	0.4655	0.0015	0.31	0.22
O(2)	0.0596	0.0009	0.9056	0.0012	0.4753	0.0015	0.43	0.22
O(3)	0.4294	0.0008	0.8416	0.0011	0.0173	0.0015	0.69	0.20
O(4)	0.4569	0.0009	0.3378	0.0011	0.0274	0.0015	0.78	0.21
O(5)	0.0251	0.0012	0.0478	0.0014	0.2395	0.0017	0.60	0.23
O(6)	0.0445	0.0012	0.5542	0.0013	0.2268	0.0016	0.69	0.24
O(7)	0.4706	0.0012	0.7031	0.0014	0.2647	0.0018	0.27	0.27
O(8)	0.4681	0.0013	0.2020	0.0015	0.2651	0.0019	0.74	0.29
O(9)	0.1714	0.0010	0.8490	0.0010	0.3116	0.0013	0.10	0.21
O(10)	0.1688	0.0011	0.3595	0.0010	0.3197	0.0014	0.20	0.22
O(11)	0.3254	0.0010	0.3841	0.0009	0.1674	0.0013	0.87	0.21
O(12)	0.3402	0.0010	0.9057	0.0009	0.2022	0.0012	0.57	0.19
O(13)	0.1189	0.0017	0.7277	0.0018	0.4736	0.0025	0.69	0.36
O(14)	0.1151	0.0017	0.2328	0.0019	0.4749	0.0026	0.80	0.36
O(15)	0.3878	0.0016	0.0208	0.0018	0.0268	0.0024	0.66	0.34
O(16)	0.3806	0.0016	0.5116	0.0017	0.0171	0.0024	0.64	0.34
O(17)*	0.2565	0.0007	0.0313	0.0007	0.4354	0.0010	0.36	0.17
O(18)*	0.2057	0.0008	0.1613	0.0007	0.1907	0.0010	0.68	0.18
O(19)*	0.2405	0.0007	0.7204	0.0007	0.0699	0.0011	0.55	0.18
O(20)*	0.3023	0.0008	0.5822	0.0007	0.3110	0.0011	0.72	0.18

* OH-oxygen atoms.

were varied until convergence was achieved. After refinement of the B 's, the model gave an R of 4.5% for these 758 F_o 's.

Then the restrictions on parameter interaction were removed to allow full-matrix refinement. Only a few cycles were required to give convergence for the scale factor and coordinates and, in separate cycles, for the B 's. The scale factor and coordinates, and then the B 's, were varied for a final cycle each. The shifts from the positions and B 's obtained with the interaction restraints were quite small,

Table 2. *Positional coordinates and isotropic temperature factors for triploidite resulting from refinement with all F_o 's*

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
M(1)	0.1872	0.0002	0.4784	0.0002	0.1882	0.0003	0.40 Å ²	0.05 Å ²
M(2)	0.1969	0.0002	0.9968	0.0002	0.2102	0.0003	0.80	0.05
M(3)	0.3046	0.0002	0.7518	0.0002	0.2958	0.0003	0.74	0.05
M(4)	0.3183	0.0002	0.2696	0.0002	0.3086	0.0003	0.50	0.05
M(5)	0.0972	0.0002	0.0710	0.0002	0.4660	0.0003	0.21	0.05
M(6)	0.0835	0.0002	0.5748	0.0002	0.4447	0.0003	0.26	0.05
M(7)	0.3939	0.0002	0.6746	0.0002	0.0343	0.0003	0.21	0.04
M(8)	0.4230	0.0002	0.1780	0.0002	0.0448	0.0003	0.54	0.04
P(1)	0.0782	0.0004	0.8219	0.0004	0.3791	0.0005	0.42	0.08
P(2)	0.0746	0.0004	0.3268	0.0004	0.3824	0.0005	0.38	0.08
P(3)	0.4233	0.0004	0.4224	0.0004	0.1144	0.0005	0.34	0.08
P(4)	0.4242	0.0004	0.9280	0.0004	0.1200	0.0005	0.39	0.08
O(1)	0.0476	0.0007	0.4131	0.0008	0.4659	0.0009	0.38	0.16
O(2)	0.0599	0.0007	0.9054	0.0008	0.4757	0.0010	0.57	0.17
O(3)	0.4300	0.0006	0.8412	0.0007	0.0177	0.0009	0.64	0.15
O(4)	0.4571	0.0006	0.3375	0.0008	0.0279	0.0009	0.70	0.15
O(5)	0.0254	0.0007	0.0472	0.0008	0.2385	0.0010	0.81	0.17
O(6)	0.0450	0.0007	0.5536	0.0008	0.2261	0.0010	0.67	0.16
O(7)	0.4706	0.0008	0.7025	0.0009	0.2639	0.0010	0.16	0.19
O(8)	0.4684	0.0008	0.2014	0.0009	0.2640	0.0011	0.59	0.20
O(9)	0.1718	0.0007	0.8491	0.0007	0.3119	0.0009	0.29	0.16
O(10)	0.1694	0.0007	0.3593	0.0007	0.3195	0.0009	0.34	0.17
O(11)	0.3254	0.0007	0.3840	0.0006	0.1674	0.0008	0.63	0.15
O(12)	0.3402	0.0007	0.9053	0.0006	0.2023	0.0008	0.47	0.14
O(13)	0.1191	0.0009	0.7280	0.0010	0.4740	0.0012	0.78	0.22
O(14)	0.1154	0.0009	0.2333	0.0010	0.4768	0.0012	0.68	0.22
O(15)	0.3878	0.0009	0.0215	0.0009	0.0284	0.0011	0.66	0.20
O(16)	0.3808	0.0009	0.5120	0.0009	0.0183	0.0011	0.68	0.21
O(17)*	0.2565	0.0005	0.0313	0.0005	0.4354	0.0007	0.31	0.13
O(18)*	0.2053	0.0006	0.1612	0.0005	0.1911	0.0007	0.61	0.13
O(19)*	0.2410	0.0005	0.7205	0.0005	0.0693	0.0007	0.53	0.13
O(20)*	0.3024	0.0006	0.5823	0.0005	0.3117	0.0007	0.69	0.14

* OH-oxygen atoms.

within a standard deviation. The R value for the 758 F_o 's used in the refinement was 4.5%, but was increased to 5.7% when the eleven reflections displaying extinction were added. Table 1 gives the coordinates and isotropic B 's, along with their standard deviations. All atoms occupy the general position $4e$. The OH-oxygen atoms are O(17) to O(20).

At the present time there appears to be no general consensus regarding the inclusion of unobserved reflections in the least-squares refinement. In triploidite 35% of the reflections had intensities below the limit of measurement, I_{\min} , and in addition 10% had intensities only slightly above this limit. A few cycles of refinement were performed using all 1417 reflections to determine if significant changes would result from the inclusion of the 648 additional F_o 's. The eleven reflections suffering from extinction were given zero weight. At convergence this model gave an R of 9.1% for the entire set of 1417 reflections; again the R was only 5.7% for the 769 reflections for which $I > 1.2 I_{\min}$. The weighted R was 5.5%. The coordinates and isotropic B 's are given in Table 2. A comparison of the parameters of Tables 1 and 2 shows that the inclusion of the unobserved and very weak reflections made little change in the model.

The difference map based upon this latter model was featureless except for random fluctuations. The location of the hydrogen atoms could not be determined.

Since the difference map gave no indication of anisotropic thermal motion, no attempt was made at anisotropic refinement. Further, the physical meaningfulness of the results of such a refinement would probably have been questionable, since it would have required 289 parameters to be varied on the basis of only 758 reflections which had reliable amplitudes.

As seen from Table 3, the shifts of atoms found in triploidite as compared with locations of atoms in the average, or triplite, structure were small; the largest was 0.56 Å. Because of this, the correlation coefficients between atoms related by pseudosymmetry elements remained high during the refinement. For OH the correlation was negligible. But for P(1) to P(4) and also for O(13) to O(16) the shifts from the positions found in triplite were quite small, namely 0.03 to 0.11 Å; so between corresponding parameters (for example between $x_{P(1)}$, $x_{P(2)}$, $x_{P(3)}$ and $x_{P(4)}$) the correlations were high with coefficients from 0.56 to 0.82 and an average of 0.67. For other atoms related by pseudosymmetry, corresponding variables had coefficients which

Table 3. *Positional differences between triploidite and triplite*
 The differences were calculated as the coordinates of triploidite minus the coordinates of triplite, as referred to a triploidite-type cell

Atom	Coordinate differences			Distance shift
	Δx	Δy	Δz	
M(1)	- 0.0055	- 0.0123	- 0.0040	0.18 Å
M(2)	0.0042	0.0061	0.0180	0.19
M(3)	- 0.0027	- 0.0075	- 0.0120	0.15
M(4)	0.0110	0.0103	0.0007	0.19
M(5)	0.0041	- 0.0011	0.0156	0.15
M(6)	- 0.0096	0.0027	- 0.0056	0.12
M(7)	- 0.0130	- 0.0033	- 0.0154	0.19
M(8)	0.0161	0.0001	- 0.0049	0.19
P(1)	0.0039	- 0.0053	- 0.0007	0.08
P(2)	0.0003	- 0.0005	0.0026	0.03
P(3)	- 0.0024	- 0.0003	- 0.0058	0.06
P(4)	- 0.0015	0.0053	- 0.0002	0.07
O(1)	- 0.0080	- 0.0020	- 0.0093	0.12
O(2)	0.0043	- 0.0097	0.0005	0.14
O(3)	- 0.0144	0.0063	- 0.0071	0.19
O(4)	0.0127	0.0026	0.0031	0.16
O(5)	- 0.0141	- 0.0061	0.0051	0.18
O(6)	0.0055	0.0003	- 0.0073	0.08
O(7)	0.0100	0.0058	- 0.0027	0.14
O(8)	0.0078	0.0047	- 0.0026	0.11
O(9)	0.0045	- 0.0071	0.0029	0.11
O(10)	0.0021	0.0031	0.0104	0.11
O(11)	- 0.0073	- 0.0097	- 0.0235	0.26
O(12)	0.0075	0.0115	0.0114	0.20
O(13)	0.0026	- 0.0035	0.0001	0.06
O(14)	- 0.0011	0.0018	0.0029	0.04
O(15)	0.0043	0.0030	0.0023	0.06
O(16)	- 0.0027	- 0.0065	- 0.0078	0.11
O(17)	- 0.0026	- 0.0300	0.0407	0.56
O(18)	- 0.0161	- 0.0041	0.0432	0.42
O(19)	0.0001	0.0318	- 0.0360	0.55
O(20)	0.0238	- 0.0024	- 0.0403	0.42

ranged from 0.21 to 0.79 and averaged 0.44. It was because of these high-correlation coefficients that parameter-interaction restraints were used until the final phase of refinement.

Table 4 lists the amplitudes of the observed and calculated structure factors for triploidite. The unobserved reflections are indicated, as are the eleven F_o 's given zero weight during the refinement because of extinction effects.

Table 4. Observed and calculated structure factor amplitudes for triploidite
The symbol * indicates an unobserved reflection while + indicates a reflection displaying extinction

Table with 12 columns: h k l, |F_o|, |F_c| for each of the six permutations of (h, k, l). Values range from approximately 0 to 800. Asterisks indicate unobserved reflections, and plus signs indicate reflections with extinction.

Table 4. (Continued)

h k l	$ F_o $	$ F_c $	h k l	$ F_o $	$ F_c $	h k l	$ F_o $	$ F_c $	h k l	$ F_o $	$ F_c $	h k l	$ F_o $	$ F_c $	
7 6 0	56.0	55.9	4 7 -8	13.5	12.6	1 8 1	21.3	20.8	8 8 -2	22.3	13.9	7 9 -4	64.2	61.2	
1 * 9.3	10.0		-7	25.0	21.8	2 * 7.8	7.4		-1 * 7.2	3.4		-3 * 7.2	7.9		
2 * 97.4	94.9		-6	35.0	33.6	3 * 80.9	79.8		0	27.0	20.9	-2 * 7.1	3.1		
3 * 7.9	5.9		-5	77.9	78.1	4 * 9.0	3.4		1 * 6.2	1.5		-1	32.8	32.5	
4 * 6.3	9.4		-4 * 10.4	12.0		5 * 8.8	7.3		9 8 -4 * 6.0	9.0		0	64.4	62.5	
8 6 -7	263.4	272.6	-3	19.5	19.0	6 * 7.7	10.4		-3	22.8	19.6	1 * 6.1	4.9		
-6	18.7	16.7	-2 * 8.9	2.5		2 8 -7 * 7.4	4.5		-2 * 6.2	5.9		2	16.0	16.4	
-5	42.3	39.1	-1	97.2	93.6	-6	74.5	69.4	-1	127.9	125.9	8 9 -4	48.3	45.6	
-4 * 10.0	4.4		0	25.3	26.1	-5 * 9.3	1.3		0 9	1	58.7	56.7	-3	16.6	15.5
-3	77.6	75.0	1	21.3	21.1	-4	37.1	38.4	2 * 6.6	0.6		-2 * 6.1	7.7		
-2 * 9.4	6.6		2 * 9.4	6.7		-3 * 8.6	8.8		3	10.9	9.4	-1	16.2	16.8	
-1	37.2	35.8	3	47.7	47.9	-2	248.1	233.8	4	70.7	72.8	0	27.9	26.7	
0 * 8.9	12.9		4	35.3	35.0	-1	10.7	7.7	5	20.2	20.3	0 10 1	54.2	55.4	
1	47.8	45.0	5	27.6	28.5	0	279.2	286.3	6	35.7	39.0	2	5.9	4.8	
2	18.5	22.5	6	24.4	22.4	1	10.6	4.3	1 9 -6	37.8	37.4	3	75.4	71.5	
3	13.2	15.2	5 7 -7	52.9	51.2	2	116.1	115.7	-5	28.1	27.1	4 * 6.8	3.3		
9 6 -6	37.8	34.7	-6 * 9.8	8.0		3 * 9.1	4.7		-4	57.5	57.2	5	70.7	62.2	
-5 * 8.7	11.8		-5	64.5	61.1	4	85.4	83.8	-3	16.6	16.8	1 10 -5 * 6.6	0.9		
-4	50.3	45.8	-4 * 10.4	8.7		5 * 8.4	4.9		-2	9.8	8.4	-4	153.3	147.3	
-3	13.8	17.9	-3	36.9	36.0	6	31.5	26.3	-1	29.6	27.2	-3 * 6.7	0.6		
-2	97.2	90.9	-2	41.9	39.6	3 8 -7	111.5	111.6	0	26.4	29.5	-2	146.3	132.6	
-1 * 8.2	13.7		-1	26.9	25.9	0 * 8.7	7.4		1	35.7	33.2	-1 * 4.6	1.6		
0	90.9	88.6	0 * 8.7	7.4		-5	86.2	81.1	2	23.6	24.6	0	83.0	75.4	
1 * 6.9	4.7		1	25.9	31.6	-4 * 9.8	1.2		3	24.9	22.7	1 * 5.2	7.9		
2	52.9	53.9	2 * 9.2	6.4		-3	40.5	39.0	4	19.0	20.3	2	26.3	24.8	
10 6 -5	213.8	206.6	3	78.0	76.9	-2 * 7.8	0.5		5	24.4	23.8	3 * 6.8	0.6		
-4	29.5	24.0	4	58.5	59.5	-1	37.8	29.7	6	56.5	56.7	4	12.6	10.1	
-3	54.2	51.6	5 * 6.4	7.4		0 * 7.1	5.4		2 9 -6 * 7.3	6.1	5	9.9	12.4		
-2	11.9	11.7	6 7 -7	13.6	10.4	1	272.3	268.7	-5 * 8.1	6.6	2 10 -6 * 5.5	1.8			
-1	38.5	35.6	-6 * 9.3	11.5		2 * 8.6	3.5		-4	56.5	45.7	-2	85.3	86.5	
0 * 5.9	5.7		-5	54.0	51.0	3	47.1	43.1	-3	16.3	14.4	-4 * 7.0	2.8		
0 7 1	76.2	76.5	-4	16.9	15.7	4 * 8.7	3.0		-2	19.0	17.2	-3	44.2	42.5	
2	13.5	11.8	-3	35.7	32.6	5	10.7	2.1	-1	24.7	22.9	-2 * 6.3	9.6		
3	13.1	12.7	-2	67.6	66.2	6 * 5.7	0.8		-1	37.5	37.0	-1	36.0	35.9	
4	35.9	36.3	-1	39.0	36.3	4 8 -7 * 7.3	0.6		1	15.9	17.5	0 * 5.3	49.1		
5	46.7	45.3	0	31.5	30.7	-6	106.8	100.3	2	40.0	42.9	1	59.4	53.5	
6	18.1	15.0	1 * 8.9	7.3		-5 * 9.4	0.7		3	22.6	19.1	2	67.7	2.1	
7	29.6	29.4	2 * 8.8	7.0		4	170.4	159.6	4 * 7.8	8.2	3	57.0	54.6		
1 7 -7	20.9	21.3	3	103.5	104.1	-3 * 9.1	1.5		5	22.6	21.3	4 * 6.3	3.7		
-6	32.7	32.6	4	49.9	50.8	-2	184.6	177.4	3 9 -6 * 7.3	7.2	5	72.9	69.1		
-5	75.4	74.8	7 7 -7	28.7	28.6	-1 * 8.2	9.9		-5	15.2	13.1	3 10 -6	27.1	25.8	
-4	37.1	35.9	-6 * 8.6	1.6		0	67.3	70.0	-4 * 8.7	5.8	-5 * 6.6	5.2			
-3	46.5	46.5	-5	15.3	11.6	1 * 8.2	2.9		-3 * 8.2	1.4	-4	43.2	42.3		
-2	18.4	18.2	-4 * 10.1	9.1		2	42.0	30.9	-2	36.6	36.8	-3 * 7.1	1.8		
-1	97.3	93.3	-3 * 9.7	54.9		3 * 8.9	4.4		-1	16.2	15.8	-2	139.3	130.1	
0 * 4.6	9.8		-2	18.2	17.6	4	179.7	181.3	0	10.1	15.0	-1 * 6.2	7.9		
1	52.5	49.6	-1	36.5	35.7	5	9.1	12.4	1 * 7.3	2.4	0	49.8	46.9		
2	25.9	25.4	0	19.4	18.9	5 8 -7	12.5	17.0	2	57.4	57.6	1 * 6.4	3.7		
3 * 9.0	11.9		1	22.0	22.6	-6 * 8.3	6.5		3	27.2	25.0	2	76.8	77.2	
4	29.6	29.7	2	30.2	30.7	-5	136.5	127.0	4	12.5	10.6	3	6.6	6.0	
5	21.9	21.9	3	53.9	53.8	-4 * 9.6	4.6		5	8.3	6.7	4	191.9	194.9	
6	20.9	21.6	8 7 -6	35.9	38.1	-3	212.6	198.7	4 9 -6	19.0	16.9	4 10 -5	79.2	73.9	
7	11.4	10.2	-5 * 8.6	2.6		-2 * 9.0	9.1		-5 * 7.9	7.1	-4 * 7.3	0.8			
2 7 -8	6.7	4.1	-4 * 8.6	19.9		-1	39.0	35.4	-4 * 8.6	5.0	-3	65.8	60.2		
-7	24.1	23.2	-3	21.3	16.7	0 * 8.2	2.7		-2	24.2	22.7	-2 * 6.9	2.3		
-6	19.2	17.9	-2 * 8.6	1.3		1	16.4	15.3	-2	42.2	43.4	-1	102.0	95.4	
-5	25.4	25.7	-1 * 8.4	7.0		2 * 8.4	1.5		-1 * 7.5	3.8	0 * 6.4	6.0			
-4	48.5	48.8	0 * 7.9	2.7		3	25.6	23.9	0 * 7.2	5.2	1	39.9	34.6		
-3	65.9	62.9	1 * 46.5	47.5		4 * 6.8	2.6		1	18.2	17.5	2 * 6.5	1.8		
-2	16.1	15.2	2	47.7	46.1	6 8 -7 * 6.3	6.7		2	40.5	39.9	3	70.2	64.3	
-1	75.5	72.2	9 7 -5 * 7.0	9.3		-6	36.8	26.6	3	32.9	31.6	5 10 -5	17.4	15.6	
0	30.8	29.6	-4	18.5	19.5	-5 * 9.3	6.1		4	22.5	23.8	-4	92.8	87.4	
1	22.9	23.1	-3	62.4	64.8	-4	97.7	96.0	5 9 -6	10.2	10.1	-3 * 7.0	1.1		
2	14.0	14.7	-2 * 7.4	3.5		-3 * 9.3	1.6		-5	38.9	37.9	-2	26.5	19.8	
3	15.8	14.0	-1 * 7.1	8.5		-2	114.1	104.5	-4 * 8.4	8.7	-1 * 6.5	5.3			
4	28.8	27.8	0 * 6.6	3.8		-1 * 8.4	6.7		-3	21.1	19.7	0	108.0	102.5	
5	45.5	42.9	1	55.8	59.0	0	269.8	265.9	-2	61.9	60.8	1 * 6.2	5.0		
6	45.5	44.7	10 7 -3	89.7	91.4	1 * 8.1	14.2		-1 * 7.6	2.8	2	41.0	32.8		
7 * 6.1	5.6		-2	22.3	22.1	2	16.5	5.2	0	30.0	30.3	3	13.5	20.5	
3 7 -8	11.3	11.1	0 8 1 * 5.1	3.3		3 * 6.9	3.0		1	31.4	30.9	6 10 -5	71.2	67.9	
-7 * 9.1	10.5		2	189.0	195.1	4	8.5	6.6	2	22.4	23.0	-4 * 6.4	6.4		
-6	15.3	16.3	3 * 8.3	0.7		7 8 -6 * 7.0	8.0		3	26.0	25.0	-3	48.7	41.1	
-5	59.9	63.5	4	54.4	47.3	-5	54.3	47.8	4	40.6	41.2	-2 * 6.4	1.2		
-4	42.2	40.1	5	17.6	15.2	-4 * 8.8	0.9		6 9 -6	21.0	18.8	-1	43.3	36.8	
-3	55.7	53.3	6	93.5	92.3	-3	126.6	121.7	-5	31.5	29.4	0 * 5.9	3.3		
-2	11.7	6.3	7 * 6.4	1.6		-2 * 8.3	7.9		-4	17.5	15.4	1	9.4	6.4	
-1	90.2	85.3	1 8 -7	69.5	62.6	-1	148.9	144.1	-3	22.0	22.7	2	12.4	10.5	
0	20.6	18.2	-6 * 8.7	1.0		0	11.5	10.4	-2	57.9	58.4	7 10 -3 * 5.6	5.9		
1 * 8.2	4.4		-5	33.7	31.2	1	46.9	42.8	-1 * 7.4	4.8	-2	17.1	10.7		
2	19.0	21.7	-4 * 8.9	11.4		2 * 6.8	10.2		0	58.5	57.1	-1	11.9	14.3	
3	25.6	25.1	-3	136.0	135.9	3	22.6	20.5	3	40.2	43.7	0	47.5	45.9	
4 * 9.7	8.6		-2	10.0	6.8	8 8 -5	10.6	18.8	2	41.3	41.0				
5	51.9	53.1	-1	150.7	133.6	-4	113.4	113.1	3	29.6	30.5				
6	40.7	41.8	0 * 4.4	7.2		-3 * 7.6	10.4		7 9 -5 * 6.4	6.1					

Description of the structure

Interatomic distances and angles, based upon the model of Table 2, are given in Tables 5 and 6. Since Mn and Fe have quite similar scattering powers, they could not be distinguished; therefore, a general designation of M is used for the metal atoms.

Each P is tetrahedrally coordinated by four O's at an average distance of 1.534 Å; the corresponding average in triplite is 1.536 Å. Half the metal atoms have trigonal-bipyramidal coordination with four O's and one OH at a mean distance of 2.126 Å. The remaining metal atoms are surrounded by an octahedron of four O's and two

Table 5. *Interatomic distances in triploidite*

The primed atoms are related to the unprimed ones by symmetry

Atoms	Distance	σ	Atoms	Distance	σ
M(1) trigonal bipyramid:			M(5) octahedron:		
M(1)–O(6)	2.156 Å	0.009 Å	M(5)–O(2)	2.254 Å	0.011 Å
M(1)–O(10)	2.106	0.010	M(5)–O(2)'	2.217	0.009
M(1)–O(11)	2.181	0.008	M(5)–O(5)	2.179	0.010
M(1)–O(15)'	2.140	0.011	M(5)–O(14)	2.166	0.013
M(1)–O(20)	2.084	0.008	M(5)–O(17)	2.151	0.007
Average	2.133		M(5)–O(20)'	2.175	0.007
			Average	2.190	
M(2) octahedron:			M(6) trigonal bipyramid:		
M(2)–O(5)	2.323	0.009	M(6)–O(1)	2.215	0.011
M(2)–O(9)	2.272	0.010	M(6)–O(1)'	2.084	0.009
M(2)–O(12)	2.169	0.008	M(6)–O(6)	2.094	0.009
M(2)–O(16)'	2.182	0.011	M(6)–O(13)	2.083	0.013
M(2)–O(17)	2.176	0.007	M(6)–O(17)'	2.048	0.007
M(2)–O(18)	2.197	0.008	Average	2.105	
Average	2.220				
M(3) octahedron:			M(7) octahedron:		
M(3)–O(7)	2.269	0.010	M(7)–O(3)	2.273	0.010
M(3)–O(9)	2.134	0.009	M(7)–O(4)'	2.125	0.008
M(3)–O(12)	2.339	0.009	M(7)–O(7)	2.212	0.010
M(3)–O(14)'	2.179	0.012	M(7)–O(16)	2.166	0.012
M(3)–O(19)	2.181	0.007	M(7)–O(18)'	2.200	0.007
M(3)–O(20)	2.257	0.008	M(7)–O(19)	2.116	0.007
Average	2.226		Average	2.182	
M(4) trigonal bipyramid:			M(8) trigonal bipyramid:		
M(4)–O(8)	2.232	0.011	M(8)–O(3)'	2.113	0.008
M(4)–O(10)	2.223	0.009	M(8)–O(4)	2.176	0.010
M(4)–O(11)	2.089	0.009	M(8)–O(8)	2.096	0.011
M(4)–O(13)'	2.128	0.012	M(8)–O(15)	2.119	0.013
M(4)–O(18)	2.090	0.007	M(8)–O(19)'	2.069	0.007
Average	2.152		Average	2.115	

Table 5. (Continued)

Atoms	Distance	σ	Atoms	Distance	σ
P(1) tetrahedron:			P(3) tetrahedron:		
P(1)-O(2)	1.529 Å	0.011 Å	P(3)-O(4)	1.552 Å	0.011 Å
P(1)-O(7')	1.495	0.010	P(3)-O(5)'	1.518	0.010
P(1)-O(9)	1.549	0.010	P(3)-O(11)	1.550	0.009
P(1)-O(13)	1.550	0.013	P(3)-O(16)	1.513	0.013
Average	1.531		Average	1.533	
P(2) tetrahedron:			P(4) tetrahedron:		
P(2)-O(1)	1.512	0.011	P(4)-O(3)	1.553	0.011
P(2)-O(8)'	1.511	0.011	P(4)-O(6)'	1.555	0.010
P(2)-O(10)	1.553	0.010	P(4)-O(12)	1.540	0.009
P(2)-O(14)	1.542	0.013	P(4)-O(15)	1.522	0.013
Average	1.529		Average	1.543	

OH's at an average 2.205 Å. The overall average distance between M and its surrounding anions is 2.169 Å, a value close to that of 2.178 Å in triplite. The M coordination polyhedra are quite distorted.

The smallness of the shifts found in triplodite from the positions of the average, or triplite, structure is seen in Table 3. It is further illustrated by comparing Figs. 1 and 2. Except for the OH positions, the sites of the triplodite asymmetric unit, as shown projected along b in Fig. 1, come very close to obeying the pseudosymmetry elements shown in Fig. 2*b*.

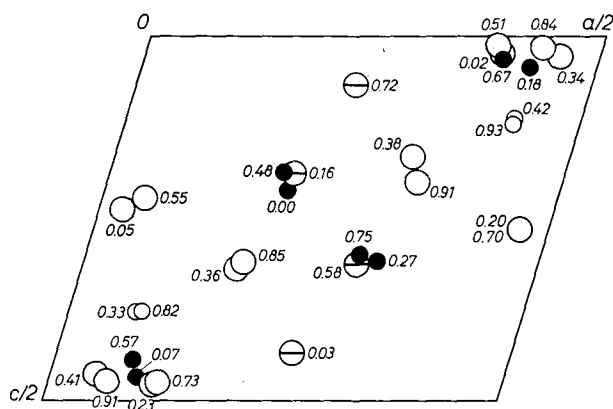


Fig. 1. Projection of triplodite along b . The locations are represented by small circles for P, shaded circles for M, large circles for O and striped circles for OH

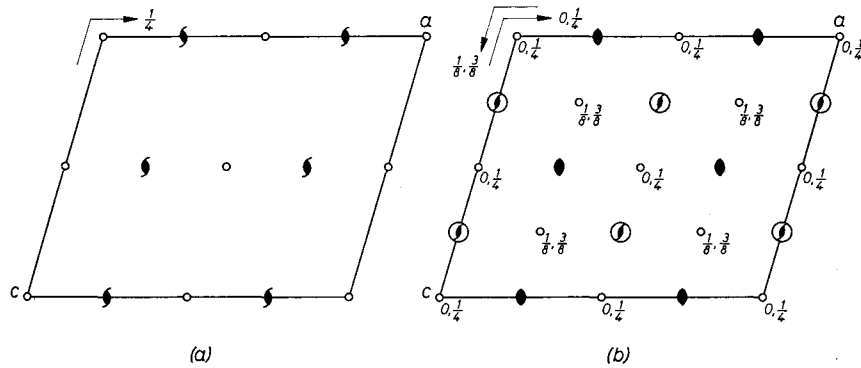


Fig. 2. (a) $P2_1/a$ symmetry elements. (b) Pseudosymmetry of triploidite, based upon $I2/a$ subcell with $b_s = \frac{1}{2}b$. The symbol \odot represents a two-fold screw axis with a translation component of $\frac{1}{2}b$ in the doubled cell

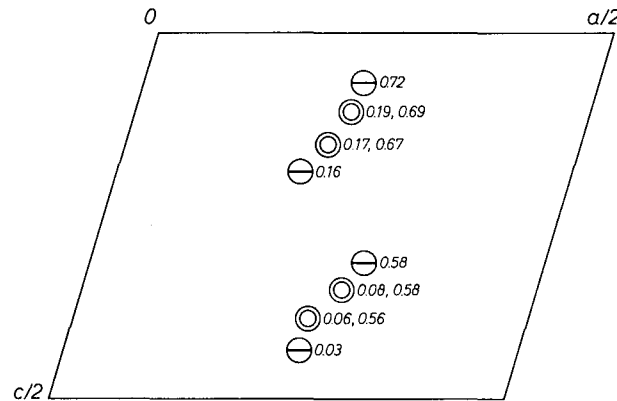


Fig. 3. Comparison of the half-occupied F sites in triplite (double circles) and the fully occupied OH sites (striped circles) in triploidite, as seen projected along b . All the y coordinates are given in terms of a triploidite-type cell

The differences between the positions of the half-occupied F sites (double circles) in triplite and those of the fully occupied OH sites (striped circles) in triploidite are shown in Fig. 3. The y coordinates of the F sites in triplite are given in terms of the triploidite cell.

In contrast to triplite, in which all metal atoms are octahedrally coordinated, the small displacements found in triploidite are sufficient to reduce the coordination numbers of M(1), M(4), M(6) and M(8) from 6 to 5. The largest contribution to this change comes from the shifts in the OH positions. As a result of the reduced coordination

Table 6. *Interatomic angles in triploidite*

Atoms	Angle	σ	Atoms	Angle	σ
O(6)–M(1)–O(10)	89.4°	0.4°	O(10)–M(4)–O(11)	81.6°	0.3°
O(6)–M(1)–O(11)	171.6	0.3	O(10)–M(4)–O(13)′	97.6	0.4
O(6)–M(1)–O(15)′	86.1	0.4	O(10)–M(4)–O(18)	88.7	0.3
O(6)–M(1)–O(20)	92.0	0.3	O(11)–M(4)–O(13)′	142.5	0.4
O(10)–M(1)–O(11)	82.2	0.3	O(11)–M(4)–O(18)	106.7	0.3
O(10)–M(1)–O(15)′	136.7	0.4	O(13)′–M(4)–O(18)	110.9	0.4
O(10)–M(1)–O(20)	108.4	0.3	O(2)′–M(5)–O(2)	85.3	0.5
O(11)–M(1)–O(15)′	99.4	0.4	O(2)′–M(5)–O(5)	100.7	0.4
O(11)–M(1)–O(20)	91.4	0.3	O(2)′–M(5)–O(14)	86.1	0.4
O(15)′–M(1)–O(20)	114.7	0.4	O(2)′–M(5)–O(17)	171.2	0.3
O(5)–M(2)–O(9)	86.4	0.3	O(2)′–M(5)–O(20)′	89.6	0.3
O(5)–M(2)–O(12)	162.2	0.3	O(2)–M(5)–O(5)	83.1	0.3
O(5)–M(2)–O(16)′	88.7	0.4	O(2)–M(5)–O(14)	170.9	0.4
O(5)–M(2)–O(17)	81.0	0.3	O(2)–M(5)–O(17)	88.6	0.3
O(5)–M(2)–O(18)	78.1	0.3	O(2)–M(5)–O(20)′	94.8	0.3
O(9)–M(2)–O(12)	76.1	0.3	O(5)–M(5)–O(14)	101.4	0.4
O(9)–M(2)–O(16)′	117.8	0.4	O(5)–M(5)–O(17)	84.9	0.4
O(9)–M(2)–O(17)	76.9	0.3	O(5)–M(5)–O(20)′	169.2	0.3
O(9)–M(2)–O(18)	155.9	0.3	O(14)–M(5)–O(17)	99.5	0.4
O(12)–M(2)–O(16)′	96.5	0.4	O(14)–M(5)–O(20)′	82.1	0.4
O(12)–M(2)–O(17)	97.9	0.3	O(17)–M(5)–O(20)′	84.5	0.3
O(12)–M(2)–O(18)	119.5	0.3	O(1)–M(6)–O(1)′	80.2	0.5
O(16)′–M(2)–O(17)	161.7	0.4	O(1)–M(6)–O(6)	88.9	0.3
O(16)′–M(2)–O(18)	80.5	0.3	O(1)–M(6)–O(13)	166.7	0.5
O(17)–M(2)–O(18)	82.5	0.3	O(1)–M(6)–O(17)′	81.8	0.3
O(7)–M(3)–O(9)	159.4	0.4	O(1)′–M(6)–O(6)	119.9	0.4
O(7)–M(3)–O(12)	84.5	0.3	O(1)′–M(6)–O(13)	91.4	0.4
O(7)–M(3)–O(14)′	88.6	0.4	O(1)′–M(6)–O(17)′	120.8	0.3
O(7)–M(3)–O(19)	81.4	0.4	O(6)–M(6)–O(13)	104.2	0.4
O(7)–M(3)–O(20)	75.7	0.3	O(6)–M(6)–O(17)′	115.5	0.4
O(9)–M(3)–O(12)	75.4	0.3	O(13)–M(6)–O(17)′	94.0	0.4
O(9)–M(3)–O(14)′	95.8	0.4	O(3)–M(7)–O(4)′	81.1	0.3
O(9)–M(3)–O(19)	99.0	0.3	O(3)–M(7)–O(7)	83.2	0.4
O(9)–M(3)–O(20)	124.9	0.3	O(3)–M(7)–O(16)	167.5	0.4
O(12)–M(3)–O(14)′	115.4	0.4	O(3)–M(7)–O(18)′	93.7	0.3
O(12)–M(3)–O(19)	78.9	0.3	O(3)–M(7)–O(19)	86.4	0.3
O(12)–M(3)–O(20)	154.8	0.3	O(4)′–M(7)–O(7)	100.5	0.4
O(14)′–M(3)–O(19)	161.8	0.4	O(4)′–M(7)–O(16)	87.4	0.4
O(14)′–M(3)–O(20)	80.0	0.3	O(4)′–M(7)–O(18)′	87.4	0.3
O(19)–M(3)–O(20)	82.8	0.3	O(4)′–M(7)–O(19)	165.9	0.3
O(8)–M(4)–O(10)	168.6	0.4	O(7)–M(7)–O(16)	104.0	0.4
O(8)–M(4)–O(11)	87.1	0.4	O(7)–M(7)–O(18)′	170.8	0.3
O(8)–M(4)–O(13)′	92.0	0.5	O(7)–M(7)–O(19)	84.2	0.4
O(8)–M(4)–O(18)	93.5	0.4	O(16)–M(7)–O(18)′	80.8	0.3

Table 6. (Continued)

Atoms	Angle	σ	Atoms	Angle	σ
O(16)–M(7)–O(19)	104.4°	0.4°	O(1)–P(2)–O(8)′	109.2°	0.6°
O(18)′–M(7)–O(19)	87.0	0.3	O(1)–P(2)–O(10)	109.6	0.6
O(3)′–M(8)–O(4)	83.7	0.3	O(1)–P(2)–O(14)	111.2	0.7
O(3)′–M(8)–O(8)	110.4	0.4	O(8)′–P(2)–O(10)	109.7	0.6
O(3)′–M(8)–O(15)	91.9	0.4	O(8)′–P(2)–O(14)	108.3	0.7
O(3)′–M(8)–O(19)′	131.1	0.3	O(10)–P(2)–O(14)	108.9	0.6
O(4)–M(8)–O(8)	86.6	0.3	O(4)–P(3)–O(5)′	110.1	0.6
O(4)–M(8)–O(15)	171.4	0.4	O(4)–P(3)–O(11)	108.9	0.5
O(4)–M(8)–O(19)′	82.7	0.3	O(4)–P(3)–O(16)	108.8	0.6
O(8)–M(8)–O(15)	101.9	0.4	O(5)′–P(3)–O(11)	110.5	0.5
O(8)–M(8)–O(19)′	115.3	0.4	O(5)′–P(3)–O(16)	109.9	0.6
O(15)–M(8)–O(19)′	94.7	0.4	O(11)–P(3)–O(16)	108.6	0.6
O(2)–P(1)–O(7)′	111.6	0.6	O(3)–P(4)–O(6)′	109.3	0.6
O(2)–P(1)–O(9)	112.3	0.6	O(3)–P(4)–O(12)	112.3	0.6
O(2)–P(1)–O(13)	106.5	0.6	O(3)–P(4)–O(15)	106.2	0.6
O(7)′–P(1)–O(9)	109.1	0.6	O(6)′–P(4)–O(12)	109.6	0.5
O(7)′–P(1)–O(13)	109.5	0.6	O(6)′–P(4)–O(15)	108.6	0.6
O(9)–P(1)–O(13)	107.7	0.6	O(12)–P(4)–O(15)	110.8	0.6

number for half of the metal atoms, there are no longer infinite chains parallel to a and b made up of octahedra with shared edges. Instead, in triploidite the linkage between adjacent polyhedra alternates along the chain between a shared edge and a shared vertex.

Triplite and triploidite

Thus, the structures of triplite and triploidite are similar in most respects. The primary differences lie in very small shifts in atomic positions and in the ordering of the F or OH sites. In triplite the F atoms appear to be completely disordered between two eight-fold equipoints so that each site can be considered to be half-filled on the average. In triploidite the evidence indicates that the OH sites are completely ordered. This requires a doubling of the cell volume; so, of the 32 OH positions corresponding to a doubled triplite cell, 16 are fully occupied while 16 are vacant.

The ordering and the small differences in positions combine to allow a change in the environment of the F, OH site. In triplite each F has three M neighbors at an average distance of 2.1 Å and an additional M at about 2.8 Å to give a distorted tetrahedral coordination, as shown in Fig. 4*a*. In triploidite each OH is surrounded by

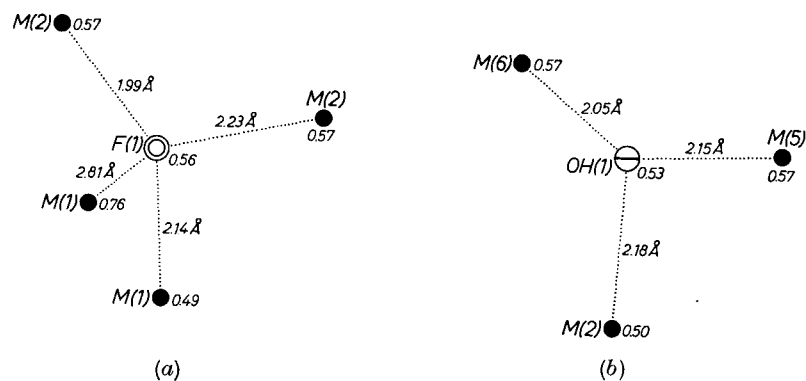


Fig. 4. (a) The environment of an F site in triplite. The y coordinates are given in terms of a triploidite-type cell. (b) The environment of an OH site in triploidite

a triangle of metal atoms at an average of 2.1 Å, as shown by the example in Fig. 4*b*. It is likely that the OH is oriented with its axis perpendicular to the plane of the triangle, as observed in hydroxyapatite (KAY, YOUNG and POSNER, 1964), so that the H is out of the plane of the metal atoms in order to reduce the repulsion between the H and the metal atoms. Since the arrangement of the metal atoms around the F site in triplite is tetrahedral, no such mechanism for reducing repulsion is possible if OH were substituted for F in that structure, a fact which probably accounts for the negligible amount of substitution observed.

Other minerals of the triplite-triploidite group

STRUNZ (1966) includes the following minerals in the triplite-triploidite group:

- triplite, $(\text{Mn, Fe})_2\text{PO}_4(\text{F})$;
- zwieselite or iron-rich triplite, $(\text{Fe, Mn})_2\text{PO}_4(\text{F})$;
- triploidite, $(\text{Mn, Fe})_2\text{PO}_4(\text{OH})$;
- wolfeite or iron-rich triploidite, $(\text{Fe, Mn})_2\text{PO}_4(\text{OH})$;
- wagnerite, $\text{Mg}_2\text{PO}_4(\text{F})$;
- sarkinite, $\text{Mn}_2\text{AsO}_4(\text{OH})$.

On the basis of unit-cell data, these minerals can be divided into two subgroups: one containing triplite and zwieselite, with b axis of 6.5 Å and symmetry $I2/a$, and the other containing triploidite, wolfeite, wagnerite and sarkinite, with b axis of 13.3 Å and symmetry $P2_1/a$. This subdivision is also supported by a comparison of the reflection

intensities in precession photographs of the minerals; in general, corresponding reflections for members of a subgroup have similar intensities.

Triplite and zwieselite

Triplite and zwieselite display identical reflection intensities. Also a continuous range of Mn:Fe ratios is found between them. Thus it is likely that they are isotypic.

Triploidite, wolfeite and wagnerite

Similarly, FRONDEL (1949) has suggested isotypy between triploidite and wolfeite on the basis of the correspondence observed between their intensities and the continuous range of composition found between them. In this study a complete set of *b*-axis precession photographs was taken of a wolfeite crystal from the Palermo mine, North Groton, New Hampshire. A careful visual comparison of these wolfeite photographs with those taken of Branchville triploidite showed corresponding reflection intensities to be identical.

During the course of this investigation the structure of wagnerite was reported by CODA, GIUSEPPETTI and TADINI (1967). A comparison of their structural data with that given in this paper for triploidite shows that the two minerals are isotypic.

Sarkinite

The close relationship between the reflection intensities of triploidite and sarkinite was first recognized by HÄGELE (1938). As part of this study complete sets of *b*-axis precession photographs were made of a sarkinite crystal from Harstigen, Sweden, and of a wagnerite crystal from Werfen, Austria. The differences observed between triploidite and sarkinite intensities were approximately of the same magnitude as the differences between triploidite and wagnerite; however, a complete structural determination would be required to prove isotypy between sarkinite and triploidite.

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